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(54) Title: WELL CEMENTING METHODS AND COMPOSITIONS (57) Abstract Cement compositions and methods of cementing within subterranean formations penetrated by well bores wherein the flow properties of one or more dry particulate cementitious materials are improved and wherein the materials can be readily conveyed out of storage tanks and the like. A preferred composition of the present invention comprises a particulate flow enhancing additive dry-blended with one or more dry particulate cementitious materials, said flow enhancing additive being comprised of a particulate solid material carrying a flow inducing polar chemical, and a sufficient amount of water to form a pumpable slurry. The methods basically include the steps of dry-blending the particulate flow enhancing additive with the one or more dry particulate cementitious materials; forming a pumpable slurry using the one or more cementitious materials having the particulate flow enhancing additive blended therewith; pumping the slurry into a well bore; and then allowing the slurry to solidify within the subterranean formation.		

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WELL CEMENTING METHODS AND COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention.

The present invention provides cement compositions and methods of cementing within subterranean formations penetrated by well bores wherein the flow properties of one or more dry particulate cementitious materials used therein are improved and wherein the materials can be readily conveyed out of storage tanks and the like.

2. Description of the Prior Art.

Cementitious materials are commonly utilized in subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby pipes such as casings and liners are cemented in well bores. In performing primary cementing, a hydraulic cement composition is pumped into the annular space between the walls of the well bore and the exterior surfaces of pipe disposed therein. The cement composition is permitted to set in the annular space thereby forming an annular sheath of hardened substantially impermeable cement therein. The cement sheath physically supports and positions the pipe in the well bore and bonds the exterior surfaces of the pipe to the walls of the well bore whereby the undesirable migration of fluids between zones or formations penetrated by the well bore is prevented.

Cementitious materials such as hydraulic cements, slag, fumed silica, fly ash and the like having various particle

size distributions are often dry-blended and placed in storage tanks. The storage tanks containing the cementitious materials are also often transported by land or sea to locations where the cementitious materials are to be used. During such transportation, the cementitious materials are subjected to vibrations and as a result, the materials are tightly packed under static conditions. One or more of the cementitious materials are often of ultra-fine particle sizes, i.e., sizes in the range of from about 5 to about 100 microns, which causes the tightly packed problem to be more severe. When the cementitious materials are conveyed out of the storage tanks at the locations of use, significant portions of the tightly packed materials are often left in the storage tanks. The incomplete conveying of the materials results in costs for disposing of the materials and increased costs to the person or entity using the cementitious materials.

Cementitious materials have heretofore been treated to make them more flowable. For example, U.S. Patent No. 2,857,286 issued to Striker on October 21, 1958 discloses a process of treating Portland cement with acetic acid or a water soluble salt of acetic acid whereby the Portland cement becomes more flowable. In accordance with the Striker patent, the treatment of Portland cement with the acid or acetate is carried out either concurrently with, or subsequent to, the grinding of the cement clinker. The acid or acetate can be combined with the cement during grinding or the ground cement can be treated by injecting the acid or acetate into the

cement under pressure as a vapor in order to blow the cement and uniformly contact it with the acid or acetate.

U.S. Patent No. 3,094,425 issued to Adams et al. on June 18, 1963 discloses that most cements compacted by vibration become semi-rigid and will not flow without considerable mechanical effort to break up the compaction. This condition is known as "pack set." Further, it is stated that it is known that certain polar molecules when added to ground cement will attach to the cement particles and reduce their surface forces. In accordance with the Adams patent, a mixture of calcium acetate and lignin sulfonate is an effective grinding aid and a pack set inhibitor when added to the cement mill and interground with the cement.

U.S. Patent No. 3,615,785 issued to Moorer et al. on February 2, 1968 discloses a cement grinding aid and pack set inhibitor comprised of polyol and a water soluble salt of an aliphatic acid having no more than 3 carbon atoms.

The above described additives are difficult to handle and must be added to the cement prior to or after grinding. Since commercially available cementitious materials generally do not include such additives, they must be provided, handled and combined with ground cement by the user by spraying, mechanical mixing or other time consuming procedure.

Thus, there are continuing needs for improving the flow properties of dry particulate cementitious materials used in cement compositions for cementing in subterranean formations penetrated by well bores wherein the materials can be readily

conveyed out of storage tanks and the like.

SUMMARY OF THE INVENTION

The present invention provides cement compositions and methods of cementing within subterranean formations penetrated by wells, such as oil and gas wells, wherein the flow properties of one or more dry particulate cementitious materials used therein are improved and wherein the materials can be readily conveyed out of storage tanks and the like. Preferred methods are basically comprised of dry-blending a particulate flow enhancing additive comprised of a particulate solid material carrying a flow inducing polar chemical thereon with the cementitious materials, forming a pumpable slurry using the one or more dry particulate cementitious materials having the particulate flow enhancing additive blended therewith, pumping the slurry into a well bore penetrating the subterranean formation, and then allowing the slurry to solidify within the subterranean formation.

The particulate flow enhancing additive of this invention is easily handled, readily dry blended with cementitious materials and enhances the flow properties of the cementitious materials. The presence of the flow enhancing additive in the cementitious materials allows the cementitious materials to be mechanically or pneumatically conveyed out of storage tanks, even when they are tightly packed therein, without leaving significant portions of the cementitious materials in the storage tanks.

A preferred cement composition useful for well cementing

comprises a particulate flow enhancing additive dry-blended with one or more particulate cementitious materials selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof. The flow enhancing additive is comprised of a particulate solid material selected from the group consisting of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth carrying a flow inducing polar chemical thereon which is selected from the group consisting of polar molecule producing organic acids, their salts and acid anhydrides. The weight ratio of solid adsorbent material to flow inducing chemical in the flow enhancing additive is in the range of from about 90:10 to about 10:90, and the flow enhancing additive is blended with the cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of the cementitious materials. The cementitious materials having particulate flow enhancing additive blended therewith are preferably mixed with a sufficient amount of water to form a pumpable slurry.

A particularly preferred particulate flow enhancing additive useful in accordance with this invention is comprised of precipitated silica powder having a flow inducing chemical comprised of glacial acetic acid adsorbed thereon. The weight ratio of precipitated silica powder to the glacial acetic acid in the flow enhancing additive is in the range of from about 90:10 to about 10:90, and the additive is blended with cementitious materials in an amount in the range of from about

0.01% to about 1.0% by weight of the cementitious materials.

It is, therefore, a general object of the present invention to provide improved cement compositions and methods of cementing by enhancing the flow properties of dry particulate cementitious materials used therein.

A further object of the present invention is to enhance the rate of oil and gas well cementing by dry-blending a flow additive of the present invention with one or more dry particulate cementitious materials used in the cementing.

Other and further objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides cement compositions and methods of cementing within subterranean formations penetrated by well bores, preferably oil and gas wells used in the production of hydrocarbons, by improving the flow properties of one or more dry particulate cementitious materials used therein such as hydraulic cements, slag, fumed silica, fly ash and the like. The methods of the invention are particularly suitable for improving the flow properties of a dry particulate cementitious material or a blend of such materials which are of fine or ultra-fine particle size and are tightly packed under static conditions in a storage tank from which they must be conveyed.

This invention also provides methods of storing one or

more dry particulate cementitious materials in a storage tank, transporting the storage tank and cementitious materials therein to a location of use and then conveying the cementitious materials out of the storage tank without unintentionally leaving a significant portion of the cementitious materials in the storage tank. The term "significant portion" is used herein to mean a portion of the stored cementitious material that is above about 15% thereof by volume.

Methods of this invention are basically comprised of dry-blending a particulate flow enhancing additive comprised of a particulate solid adsorbent material having a flow inducing chemical adsorbed thereon with one or more cementitious materials. The blend of the cementitious materials and flow enhancing additive can then be placed in a storage tank and readily conveyed therefrom, either mechanically or pneumatically, without leaving a significant portion of the cementitious materials in the storage tank.

After the cementitious materials having particulate flow enhancing additive blended therewith are transferred from the storage tank, a suitable liquid known in the art, e.g., water, is added to form a pumpable slurry. Once the cementitious materials are formulated into a pumpable slurry, it is pumped into a desired location within the well bore. Cementing is usually accomplished by pumping the slurry down through a well casing. A separate fluid is then pumped into the well casing after this so that the cement slurry is forced or squeezed out

of the bottom of the casing and back up through the annulus or space between the exterior of the well casing and the well bore to the desired location. The slurry is then allowed to solidify within the subterranean formation.

A variety of particulate solid adsorbent materials can be utilized for forming the flow enhancing additive of this invention. Examples of such adsorbent materials include, but are not limited to, precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth. Of these, precipitated silica is presently preferred. The adsorbent material utilized must be capable of adsorbing the flow inducing chemical utilized.

The flow inducing chemical utilized in accordance with this invention can be any of the heretofore known chemicals which produce polar molecules that react with cementitious materials and increase their flow properties. Examples of polar molecule producing chemicals which can be utilized include, but are not limited to, organic acids such as alkyl and/or alkene carboxylic acids and sulfonic acids, salts of the foregoing acids formed with weak bases and acid anhydrides such as sulfur dioxide, carbon dioxide, sulfur trioxide, nitrogen oxides and similar compounds. The most preferred flow inducing chemical for use in accordance with this invention is glacial acetic acid. While the exact cause for the flow enhancement of cementitious materials when contacted with a flow inducing chemical of this invention is presently unknown, it is believed that polar molecules of the chemical

react with components of the cementitious materials such as tricalcium silicate to produce a particle repulsion effect in the cementitious materials.

The weight ratio of the particulate solid adsorbent material utilized to the flow inducing chemical utilized in the flow enhancing additive is generally in the range of from about 90:10 to about 10:90, more preferably from about 75:25 to about 25:75. The resulting particulate flow enhancing additive is dry-blended with one or more cementitious materials, the flow properties of which are to be improved, in an amount in the range of from about 0.01% to about 1.0% by weight of the cementitious materials, more preferably in an amount in the range of from about 0.02% to about 0.5%.

Another method of the present invention for improving the flow properties of one or more dry particulate cementitious materials is comprised of dry-blending a particulate flow enhancing additive with the cementitious materials, the additive being comprised of a particulate solid adsorbent material having a flow inducing polar molecule producing chemical adsorbed thereon.

Another method of the present invention for improving the flow properties of one or more dry particulate cementitious materials is comprised of dry-blending a particulate flow enhancing additive with the cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of the cementitious materials, the additive being comprised of a particulate solid adsorbent material having a

flow inducing chemical adsorbed thereon selected from the group of polar molecule producing organic acids, their salts and acid anhydrides.

Yet another method of the present invention for improving the flow properties of one or more dry particulate cementitious materials is comprised of dry-blending with the cementitious materials a particulate flow enhancing additive comprised of a particulate solid adsorbent material selected from the group of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth having a flow inducing chemical adsorbed thereon selected from the group of polar molecule producing organic acids, their salts and acid anhydrides, the weight ratio of the solid adsorbent material to the flow inducing chemical being in the range of from about 90:10 to about 10:90 and the flow enhancing additive being blended with the cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of the cementitious materials.

Still another method of this invention for improving the flow properties of one or more dry particulate cementitious materials is comprised of dry-blending a particulate flow enhancing additive with the cementitious materials, the additive being comprised of precipitated silica powder having a flow inducing chemical comprised of glacial acetic acid adsorbed thereon, the weight ratio of precipitated silica powder to glacial acetic acid being in the range of from about 75:25 to about 25:75 and the flow enhancing additive being

blended with the cementitious materials in an amount in the range of from about 0.02% to about 0.5% by weight of the cementitious materials.

A method of this invention for storing one or more dry particulate cementitious materials in a storage tank, transporting the storage tank and cementitious materials to a location of use and then conveying the cementitious materials out of the storage tank without unintentionally leaving a significant portion of the cementitious materials in the storage tank is comprised of dry-blending a particulate flow enhancing additive with the cementitious materials prior to placing the materials in the storage tank, the additive being comprised of a particulate solid adsorbent material having a flow inducing polar molecule producing chemical adsorbed thereon; preferably a flow inducing polar molecule producing chemical selected from the group of organic acids, their salts and acid anhydrides.

Another method of this invention for storing one or more dry particulate cementitious materials in a storage tank, transporting the storage tank and cementing materials to a location of use and then conveying the cementitious materials out of the storage tank without unintentionally leaving a significant portion of the cementitious materials in the storage tank is comprised of dry-blending with the cementitious materials a particulate flow enhancing additive comprised of a particulate solid adsorbent material selected from the group of precipitated silica, zeolite, talcum,

diatomaceous earth and fuller's earth having a flow inducing polar molecule producing chemical adsorbed thereon selected from the group of organic acids, salts thereof and acid anhydrides, the weight ratio of the solid adsorbent material to the flow inducing chemical being in the range of from about 90:10 to about 10:90 and the flow enhancing additive being blended with the cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of the cementitious materials.

Yet another method of this invention for storing one or more dry particulate cementitious materials in the storage tank, transporting the storage tank and cementitious materials to a location of use and then conveying the cementitious materials out of the storage tank without unintentionally leaving a significant portion of the cementitious materials in the storage tank is comprised of dry-blending a particulate flow enhancing additive with the cementitious materials, the additive being comprised of precipitated silica powder having a flow inducing additive comprised of glacial acetic acid adsorbed thereon, the weight ratio of precipitated silica powder to glacial acetic acid being in the range of from about 75:25 to about 25:75 and the flow enhancing additive being blended with the cementitious materials in an amount in the range of from about .02% to about 0.5% by weight of the cementitious materials.

In order to further illustrate the methods and compositions of the present invention, the following examples

are given.

Example 1

Several cement blends were prepared as shown in Table I below.

TABLE I

Test Cement Blends							
Blend No.	API Portland Cement, lb./sack of Cement	2 parts:1 part by wt. Portland Cement -Ultra Fine Cement Mixture	50%-50% Mixture of Ultra-Fine Cement and Ultra-Fine Fly Ash, % by Weight of Composition	Fumed Silica, lb./sack of Cement	Class F Pozzolan, lb./sack of Cement	Calcium Chloride, % by weight of Cement	Particulate Crystalline Silica, % by weight of Composition
1	47	-	-	18.5	18.5	1	-
2	-	-	65	-	-	-	35
3	-	98	-	-	-	2	-

The cement blends were each tested by placing a volume of each blend sufficient to achieve a packed thickness of approximately 3/4" in a 200 ml flask. The cement blend was swirled in the flask until a level cement surface was produced. The flask containing the cement blend was then placed on a vibrator and vibrated for the time period indicated in Table II below. The vibrator was an FMC Syntron Jogger, Model J-1, 115 Volts/60 Hz/1 AMP equipped with a PowerStat voltage regulator. After being vibrated, the flask containing the cement blend was removed from the vibrator and placed on a rotator for slowly rotating the flask in a vertical plane and counting the number of rotations. The flask was rotated for the number of counts required for the cement blend in the flask to decompact therein. After the

cement blend decompacted, the flask and cement blend were vigorously shaken and the cement blend was swirled for 5 seconds whereupon the test was repeated. This procedure was followed for a total of five tests or until consistent results were observed.

The above described tests were repeated at a number of higher and lower vibration frequencies (as indicated by the voltage set on the voltage regulator) and for different times until a maximum average count was determined. The results of these tests are set forth in Table II below.

TABLE II

Maximum Average Rotator Counts			
	Blend No. 1	Blend No. 2	Blend No. 3
Vibrator Voltage, volts	54	56	54
Vibration Time, seconds	20	25	20
	Rotator Counts		
1st. Test	36	30	30
2nd Test	31	22	36
3rd Test	33	31	27
4th Test	41	26	36
5th Test	21	29	38
6th Test	37	-	-
Average Count	33.2	27.6	33.4

Example 2

The cement blends described in Example 1 were combined with varying amounts of the flow enhancing additive of the present invention. The additive was comprised of precipitated silica powder and glacial acetic acid having a weight ratio of silica to acid of 1:1. The results of these tests are set forth in Table III below.

TABLE III

Test Rotator Counts When Flow Enhancing Additive Included In Cement Blends

	Blend No. 1	Blend No. 2	Blend No. 3
Vibrator Voltage, volts	54	56	54
Vibration Time, seconds	20	25	20
Quantity of Additive, % by <u>wt. of Blend</u>			
	Rotator Counts		
0	33.2	27.6	33.4
0.05	15.6	10.8	26.6
0.075	15	9	20.4
0.1	-	7.8	11.6
0.125	-	5	9.2
0.15	-	6	6.6
0.175	-	-	4.2

As can be seen from the test results given in Table III, the addition of the additive of this invention to the cement blends resulted in significant flow enhancement.

Example 3

Cement compositions suitable for use in downhole cementing were combined with varying amounts of the flow enhancing additive of the present invention. The additive was comprised of precipitated silica powder and glacial acetic acid having a weight ratio of silica to acid of 1:1. The results of these tests are set forth in Table IV below.

TABLE IV
Comparison Of Slurry Composition Properties

Blend	Additive Level % bwoc	Thickening Time hr:min	Fluid Loss cc/30min	Free Water % by Slurry volume	Rheology @75°F 300-200-100	Rheology @120°F 300-200-100	UCA Analyzer Compressive Strength @ 140°F Time to 50psi / 500psi in hr:min	Crush Test Compressive Strength (psi) @ 24hr and 80°F
No. 1	None	1:46 @ 120°F	505	0 @ 120°F	130-121-111	134-127-119	1:13 / 2:48	ND*
No. 1	0.465%	1:52 @ 120°F	450	0 @ 120°F	121-113-103	129-120-111	1:19 / 3:01	ND*
No. 2	None	4:04 @ 70°F	ND*	ND*	ND*	ND*	ND*	1496
No. 2	0.05%	4:22 @ 70°F	ND*	ND*	ND*	ND*	ND*	ND*
No. 2	0.1%	4:00 @ 70°F	ND*	ND*	ND*	ND*	ND*	1420
No. 2	0.2%	4:30 @ 70°F	ND*	ND*	ND*	ND*	ND*	1375
No. 2	0.5%	ND*	ND*	ND*	ND*	ND*	ND*	1510

Blend No. 1: Class H Portland cement; SSA-1™ fine silica flour (35% bwoc); Silicalite™ additive (20% bwoc); water (11.58 gal/sk); and density (13.8 lbs/gal).

Blend No. 2: Class A Portland cement; Micro Matrix™ cement (18% bwoc); calcium chloride (2% bwoc); foaming surfactants; synthetic sea water (6.9 gal/sk); unfoamed slurry density (15.23 lbs/gal); and foamed slurry density (12.5 lbs/gal).

* Not Determined.

As can be seen from the test results given in Table IV, the addition of the additive of this invention to the cement slurry composition resulted in no significant changes.

Example 4

Flow rates of the cementitious materials of the present invention are enhanced by dry-blending the flow additive therewith. For example, two jobs were performed using a foamed mixture of Class A cement and ultra-fine particle size cement with the appropriate surfactant blends. The slurry densities prior to foaming were identical in both cases (approximately 15.2 lbs/gal) and both jobs were performed using the same rig. The slurry pump rate of cement without the flow additive dry-blended therewith was about 5.2 barrels per minute while the slurry pump rate of cement with the flow additive dry-blended therewith was about 8.2 barrels per minute. Therefore, as can be seen from this example, the addition of the flow additive of this invention to the cementitious materials resulted in a significant increase in the slurry pump rate.

Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

What is claimed is:

1. A method of improving the flow properties of one or more dry particulate cementitious materials comprising dry-blending a particulate flow enhancing additive with said cementitious materials, said additive being comprised of a particulate solid adsorbent material having a flow inducing polar molecule producing chemical adsorbed thereon.
2. The method of claim 1 wherein said solid adsorbent material is selected from the group of precipitated silica, zeolite and talcum.
3. The method of claim 1 wherein said flow inducing chemical is selected from the group of polar molecule producing organic acids, their salts and acid anhydrides.
4. The method of claim 1 wherein the weight ratio of said solid adsorbent material to said flow inducing chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90.
5. The method of claim 4 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.
6. The method of claim 1 wherein said cementitious materials are selected from the group of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof.
7. The method of claim 6 wherein said solid adsorbent material is precipitated silica powder and said flow inducing chemical is glacial acetic acid.

8. The method of claim 7 wherein the weight ratio of said precipitated silica to said glacial acetic acid in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

9. The method of claim 8 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.02% to about 0.5% by weight of said cementitious materials.

10. A method of storing one or more dry particulate cementitious materials in a storage tank, transporting the storage tank and cementitious materials to a location of use and then conveying the cementitious materials out of the storage tank without unintentionally leaving a significant portion of the cementitious materials in the storage tank comprising dry-blending a particulate flow enhancing additive with said cementitious materials prior to placing said cementitious materials in said storage tank, said additive being comprised of a particulate solid adsorbent material having a flow inducing polar molecule producing chemical selected from the group of organic acids, their salts and acid anhydrides adsorbed thereon.

11. The method of claim 10 wherein said cementitious materials are pneumatically conveyed out of said storage tank.

12. The method of claim 10 wherein said solid adsorbent material is selected from the group of precipitated silica, zeolite and talcum.

13. The method of claim 10 wherein said flow inducing

polar molecule producing chemical is glacial acetic acid.

14. The method of claim 10 wherein the weight ratio of said solid adsorbent material to said flow inducing chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

15. The method of claim 14 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.

16. The method of claim 10 wherein said cementitious materials are selected from the group of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof.

17. A method of storing one or more dry particulate cementitious materials in a storage tank, transporting the storage tank and cementitious materials to a location of use and then conveying the cementitious materials out of the storage tank without unintentionally leaving a significant portion of the cementitious materials in the storage tank comprising dry-blending a particulate flow enhancing additive with said cementitious materials prior to placing said cementitious materials in said storage tank, said additive being comprised of precipitated silica powder having glacial acetic acid adsorbed thereon.

18. The method of claim 17 wherein said cementitious materials are pneumatically conveyed out of said storage tank.

19. The method of claim 17 wherein the weight ratio of said precipitated silica powder to said glacial acetic acid in

said flow enhancing additive is in the range of from about 90:10 to about 10:90.

20. The method of claim 19 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.

21. A method of cementing in a subterranean formation penetrated by a well bore comprising the steps of:

dry-blending a particulate flow enhancing additive with one or more dry particulate cementitious materials, said additive being comprised of a particulate solid material carrying a flow inducing polar chemical;

forming a pumpable slurry using said one or more dry particulate cementitious materials having said particulate flow enhancing additive blended therewith;

pumping the slurry into the well bore; and

allowing the slurry to solidify within the subterranean formation.

22. The method of claim 21 wherein said particulate solid material is selected from the group consisting of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth.

23. The method of claim 21 wherein said flow inducing chemical is selected from the group consisting of polar molecule producing acids, their salts and acid anhydrides.

24. The method of claim 23 wherein said polar molecule producing acids are organic acids.

25. The method of claim 21 wherein the weight ratio of said particulate solid material to said flow inducing chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

26. The method of claim 21 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.

27. The method of claim 21 wherein said cementitious materials are selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof.

28. The method of claim 27 wherein said particulate solid material is precipitated silica powder and said flow inducing chemical is glacial acetic acid.

29. The method of claim 28 wherein the weight ratio of said precipitated silica to said glacial acetic acid in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

30. The method of claim 29 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.02% to about 0.5% by weight of said cementitious materials.

31. The method of claim 21 wherein the well bore is for use in the production of hydrocarbons from the subterranean formation.

32. A method of cementing an oil or gas well comprising the steps of:

dry-blending a particulate flow enhancing additive with one or more dry particulate cementitious materials, said additive being comprised of a particulate solid material carrying a flow inducing polar chemical;

forming a pumpable slurry using said one or more dry particulate cementitious materials having said particulate flow enhancing additive blended therewith;

pumping the slurry into the well; and

allowing the slurry to solidify.

33. The method of claim 32 wherein said particulate solid material is selected from the group consisting of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth.

34. The method of claim 32 wherein said flow inducing chemical is selected from the group consisting of polar molecule producing acids, their salts and acid anhydrides.

35. The method of claim 34 wherein said polar molecule producing acids are organic acids.

36. The method of claim 32 wherein the weight ratio of said particulate solid material to said flow inducing chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

37. The method of claim 32 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.

38. The method of claim 32 wherein said cementitious

materials are selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof.

39. The method of claim 38 wherein said particulate solid material is precipitated silica powder and said flow inducing chemical is glacial acetic acid.

40. The method of claim 39 wherein the weight ratio of said precipitated silica to said glacial acetic acid in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

41. The method of claim 40 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.02% to about 0.5% by weight of said cementitious materials.

42. A method of cementing in a subterranean formation penetrated by a well bore comprising the steps of:

dry-blending precipitated silica powder carrying glacial acetic acid thereon with one or more dry particulate cementitious materials selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof;

forming a pumpable slurry using said one or more dry particulate cementitious materials blended with said precipitated silica powder having glacial acetic acid adsorbed thereon;

pumping the slurry into the well bore; and

allowing the slurry to solidify within the subterranean formation.

43. The method of claim 42 wherein the weight ratio of said precipitated silica to said glacial acetic acid in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

44. The method of claim 42 wherein said precipitated silica powder having glacial acetic acid adsorbed thereon is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.

45. A cement composition comprising:

a particulate flow enhancing additive dry-blended with one or more dry particulate cementitious materials, said flow enhancing additive being comprised of a particulate solid material carrying a flow inducing polar chemical; and

a sufficient amount of water to form a pumpable slurry.

46. The composition of claim 45 wherein said particulate solid material is selected from the group consisting of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth.

47. The composition of claim 45 wherein said flow inducing chemical is selected from the group consisting of polar molecule producing acids, their salts and acid anhydrides.

48. The composition of claim 47 wherein said polar molecule producing acids are organic acids.

49. The composition of claim 45 wherein the weight ratio of said particulate solid material to said flow inducing

chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

50. The composition of claim 45 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials.

51. The composition of claim 45 wherein said cementitious materials are selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof.

52. The composition of claim 51 wherein said particulate solid material is precipitated silica powder and said flow inducing chemical is glacial acetic acid.

53. The composition of claim 52 wherein the weight ratio of said precipitated silica to said glacial acetic acid in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

54. The composition of claim 53 wherein said flow enhancing additive is blended with said cementitious materials in an amount in the range of from about 0.02% to about 0.5% by weight of said cementitious materials.

55. A well cement composition comprising:

a particulate flow enhancing additive dry-blended with one or more particulate cementitious materials selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious

materials;

wherein said flow enhancing additive is comprised of a particulate solid material carrying a flow inducing polar chemical, said flow inducing chemical is selected from the group consisting of polar molecule producing acids, their salts and acid anhydrides; and

a sufficient amount of water to form a pumpable slurry.

56. The composition of claim 55 wherein said particulate solid material is selected from the group consisting of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth.

57. The method of claim 55 wherein said polar molecule producing acids are organic acids.

58. The composition of claim 55 wherein the weight ratio of said particulate solid material to said flow inducing chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90.

59. An oil or gas well cement composition comprising:

a particulate flow enhancing additive dry-blended with one or more particulate cementitious materials in an amount in the range of from about 0.01% to about 1.0% by weight of said cementitious materials;

wherein said cementitious materials are selected from the group consisting of hydraulic cements, slag, fumed silica, fly ash and mixtures thereof;

wherein said flow enhancing additive is comprised of a particulate solid material carrying a flow inducing polar

chemical;

wherein said particulate solid material is selected from the group consisting of precipitated silica, zeolite, talcum, diatomaceous earth and fuller's earth;

wherein said flow inducing chemical is selected from the group consisting of polar molecule producing acids, their salts and acid anhydrides;

wherein the weight ratio of said particulate solid material to said flow inducing chemical in said flow enhancing additive is in the range of from about 90:10 to about 10:90; and

a sufficient amount of water to form a pumpable slurry.

INTERNATIONAL SEARCH REPORT

Intern. Application No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B14/06 C04B20/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 198702 Derwent Publications Ltd., London, GB; Class L02, AN 1987-013997 XP002137033 & SU 1 235 845 A (TOMSK ENG CONS INST), 7 June 1986 (1986-06-07) abstract</p> <p style="text-align: center;">— -/-</p>	1,3-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/GB 00/00023

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 482 381 A (SPITZ RODNEY D ET AL) 13 November 1984 (1984-11-13)	21-23, 25-27, 31-34, 36-38, 45-47, 49-51, 55,56, 58,59
A	column 1, line 51 - line 60 column 2, line 3 - line 26 column 2, line 52 - line 66 claims 20-22	
A	US 3 094 425 A (ADAMS ALFRED B ET AL) 18 June 1963 (1963-06-18) cited in the application the whole document	1-44,48, 52-54,57
A	EP 0 507 368 A (THORS CHEM FAB AS) 7 October 1992 (1992-10-07) column 1, line 12 -column 2, line 52	1-59
A	CHEMICAL ABSTRACTS, vol. 103, no. 2, 15 July 1985 (1985-07-15) Columbus, Ohio, US; abstract no. 10508f, "Cement product with early strength" page 270; XP000183781 abstract	1
A	& JP 06 021842 A (SANYO CHEMICAL INDUSTRIES)	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
SU 1235845 A	07-06-1986	NONE	
US 4482381 A	13-11-1984	US 4569694 A	11-02-1986
US 3094425 A	18-06-1963	NONE	
EP 0507368 A	07-10-1992	AT 94855 T	15-10-1993
		DE 69200014 D	28-10-1993
		DE 69200014 T	03-03-1994
		FI 921492 A	06-10-1992
		NO 921300 A	06-10-1992
		SE 9101012 A	06-10-1992
JP 6021842 A	28-01-1994	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)

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